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## ABSTRACT

Metallic oxide thick film switches were processed on alumina substrates using thick film technology. Vanadium pentoxide in powder form was mixed with other oxides e.g., barium, strontium copper and glass frit, ground to a fine powder in a micromill and pastes and screen printable inks were made using commercial conductive vehicles and appropriate thinners. Some switching devices were processed by conventional screen printing and firing of the inks and commercial cermet conductor terminals on 96% alumina substrates while others were made by applying small beads or "dots" of the pastes between tiny platinum wires. Processing involved heat treatment at varying temperatures up to 1000 degrees C in vacuum, argon, reducing atmospheres, and air firing in a tunnel kiln. Resistance - temperature tests showed resistance changes by factors of 1000 to 10,000 at various critical temperatures between 50 and 90 degrees C. Static and dynamic volt - ampere and pulse tests performed indicate that the switching and self oscillatory characteristics of these devices could make them useful in memory element, oscillator, automatic control applications, etc.

## THEORY AND BACKGROUND

The oxide switches reported on here are based primarily on large resistance changes in vanadium oxides which occur at certain critical temperatures and/or applied voltages. Resistance anomalies and conductivity transitions in vanadium oxides have been studied extensively in the past <sup>1,2,3</sup>. In recent years an increasing interest has been manifest in the characteristics of transition oxides such as vanadium and titanium and with the advent of modern instruments and techniques greater insight into the possible causes and mechanisms of the insulator resistor-semiconductor-metal transitions exhibited by these oxides has been gained. Numerous papers and research results on this and related subjects were presented at an International Symposium on Electronic properties and applications of oxides at Purdue University on May 29--June 1, 1974.<sup>7,8,9,10</sup>

Theories based on energy bands, lattice structure deformations and defects as well as phase transitions associated with internal unit cell dimensional changes as indicated by X-Ray diffraction data have been advanced to explain the two to four or more decade changes in resistance observed at critical temperatures and applied potentials. In general, no single theory gives a complete picture of the phenomena although the causes are generally considered to be thermally, and/or electrically and magnetically induced.

In 1970 research studies and experiments were initiated on copper and vanadium oxide characteristics by Professor Leo Williams, Jr., and students in Electrical and Mechanical Engineering at North Carolina A&T State University. The objective was to study the characteristics of the metallic oxides with a view toward practical applications in electrical circuits. Vanadium oxide polycrystalline structures were produced, tested, and possible applications in sensors, switching and memory elements were discussed at the ISHM International Symposium in 1972<sup>4</sup>. However, these crystals did not lend themselves to practical processing of devices since a great deal of time was spent in selecting, and mounting crystals with the characteristics of interest. Subsequent

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research efforts were aimed at using thick film techniques to make repeatable devices for study and applications. Suggested materials and methods of preparation based upon Futaki's paper<sup>3</sup> were used in making the devices reported on in this paper. Cope and Penn<sup>5</sup> have produced some small vanadium oxide based switches based upon procedures outlined by Futaki. Bongers and Enz<sup>6</sup> have reported the production of a working model of a bistable element consisting of a small crystal of  $\text{VO}_2$  clamped between spring loaded copper contacts. This paper deals with some of the results obtained at N.C. A&T State University using thick film techniques to make practical metallic oxide switches and some applications of these devices.

#### OXIDE SWITCHING MATERIAL PREPARATION AND DEVICE FABRICATION

Commercial grades of metallic oxides and chemicals made by Fisher Scientific Company were used to make the switching materials. Either vanadic acid technical grade or certified  $\text{V}_2\text{O}_5$  (V-5 or V-7) in anhydrous powder form, was one constituent of all samples made. All materials were ground in a micromill, either individually or in mixed form to a very fine powder. The mixtures were combined with Electro-Science Laboratories (ESL) type 405 conductive vehicle and type 402 thinner to make a paste, or ink suitable for thick film printing, and applied to a 1 inch sq. alumina substrate in one of four types of configurations as shown in Fig. 1. A gold or silver conductive ink was screen printed and fired on all substrates before the application of the oxide materials. This conductive pattern facilitated electrical connections to all samples via standard sockets. Some of the samples were encapsulated in a Sears clear acrylic coating or in stycast CP-16 for protection and/or to improve thermal characteristics. Although a large variety of mixtures were processed and tested, the following three major types are reported on in this paper:

##### 1. Devices made using vanadium pentoxide only

(a) samples designated "W" were made using vanadium pentoxide which was reduced in an ammonia atmosphere at 400 degrees C for 18 hours. The powder was thereafter mixed with 5% borosilicate glass, a paste was formed and applied by

hand to the substrate as shown in Fig. 1 (a)

(b) Samples and devices designated "PW" were made using vanadium pentoxide powder and were heated in a slightly reducing Argon atmosphere, at 400 degrees C for 21 hours. A paste was formed and small dots of this paste was applied between two platinum wires (used to make electrical connections) on alumina substrates. Terminations were completed by application of ESL - 1-30 conductive paste by hand as shown in Fig. 1 (c). The substrates were thereafter heated in air at 125 degrees C.

##### 2. Binary mixtures of vanadium pentoxide and copper oxide

A 50% mixture by weight of,  $\text{V}_2\text{O}_5$  and cuprous or cupric oxide was fused, cooled, crushed and milled to a fine powder which was subsequently made into a paste and applied to the substrate as in Fig. 1 (a). These devices were designated "VC".

##### 3. Ternary mixtures with vanadium pentoxide

Mixtures consisting of 71%  $\text{V}_2\text{O}_5$ , 17% strontium carbonate and 12% ammonium phosphate monobasic were ground, compressed in 0.5 inch diameter discs at 10,000 psi and were heated in a reducing atmosphere at 400 degrees C for 19 hours. The disc was cooled, crushed, and ground and a paste was applied, as in Fig. 1(a), to alumina substrates between high temperature gold conductive terminals which were processed using ESL-5800 ink. These substrates were heated in argon gas at 550 degrees C for 16 hours and were subsequently quenched in argon. These devices were designated "F270".

Other samples of these materials were mixed with the aforementioned conductive vehicle and thinner to make an ink which was screen printed on alumina substrates using a 200 - 250 mesh steel screen in the form of the resistor pattern shown in Fig. 1(d). A manual thick film printer was used in this operation. The conductor terminations consisted of prefired ESL type 590 silver conductive ink. After printing, the oxide was dried at 150 degrees C and thereafter the substrates were submitted to a temperature of 430 degrees C for 15 hours in a reducing atmosphere.

# TEMPERATURE - RESISTANCE TESTS

The various oxide samples were placed in a temperature chamber and resistance measurements were made as the temperature was varied from room temperature in 10 degree increments up to 150 degrees C and decreased to room temperature.

Fig. 2 shows the results of temperature resistance tests on reduced V-5 and V-7 "PW" type samples. The V-7 sample shows negligible switching tendencies. The V-5 sample shows a marked 40K ohm resistance anomaly between 50 and 70 degrees C, a secondary jump between 90 degrees C and 95 degrees C, and a third jump of approximately one decade increase at 130 degrees C. Both samples show evidence of hysteresis effects. Fig. 3 shows the results of the same type samples which were heated in argon except that the V-7 sample contained glass but the V-5 sample did not. It is evident that the sample with glass has a larger resistance transition, is more stable at higher temperatures since the secondary transition at 130 degrees C is absent and therefore has a more suitable switching characteristic.

Fig. 4 indicates a negative two decade resistance change between room temperature and 35 degrees C and a positive one decade change between 100 and 105 degrees C for the binary "VC" sample consisting of fused vanadium pentoxide and cuprous oxide. As in the previous samples, all abrupt resistance changes took place during increasing temperature. The binary mixtures containing glass showed no anomalies in the temperature range investigated.

Temperature - resistance plots for three types of ternary oxide mixtures are presented in Fig. 5. As indicated in the figure, the oxide materials were applied to two substrates by hand and on one substrate the materials were screen printed in thick film ink form. Each of the substrates contained ten oxide samples, however data for only one representative sample i.e., R-3, R-1, and R-5 for each substrate appears in the plot. Several salient and interesting features are in evidence from a study of the results of this test. The printed sample had a more gradual change in resistance (490K ohm from 41 to 90 degrees C), and from 130 to 150 degrees

C it was essentially an open circuit i.e. its resistance was above 10 megohms. At a critical temperature of 130 degrees C the sample is essentially an insulator undergoing a positive resistance transition in the order of  $10^7$  or greater. Sample R-1 has the most desirable switching characteristic having almost a 3 decade resistance change in the 60 to 70 degree C temperature range. Except for the semiconductor to insulator transition exhibited in sample R-5, there are no multiple transitions as observed in the other samples, and hysteresis effects have been greatly reduced.

Within the past year, E.I. Du Pont De Nemours & Co. introduced Tyox 9253, a new vanadium oxide-based thick film switching ink which is screen printable. Samples of this composition were printed and fired and Fig. 6 presents a temperature-resistance plot of this commercially available material included herein for comparative purposes.

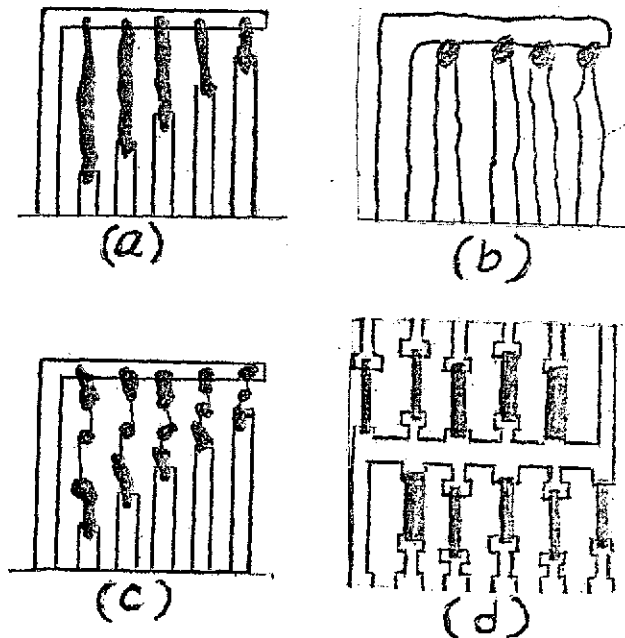


Fig. 1 Methods of applying oxides to substrates (a) and (b) by hand between printed conductors, (c) small dots between platinum wires, (d) screen printed on prefired conductors.

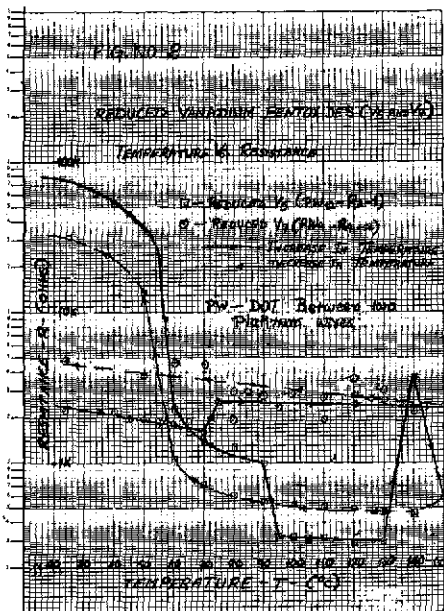


Fig. 2 Resistance-Temperature curves for V-5 and V-7 type vanadium pentoxide "PW" samples which were processed in a reducing atmosphere.

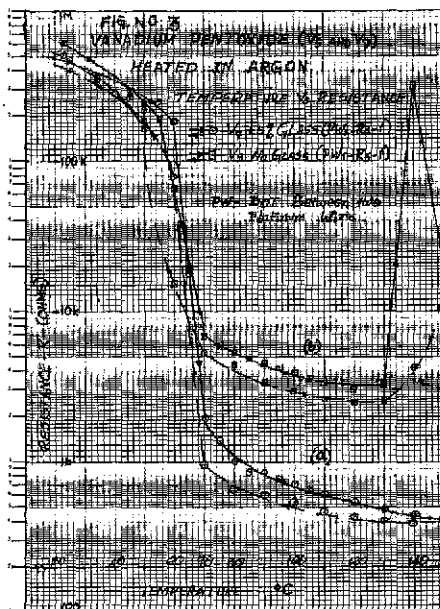


Fig. 3 Resistance-Temperature curves for "PW" vanadium pentoxide samples processed in an argon atmosphere. (a) V-7 mixed with 5% borosilicate glass (b) V-5 without glass.

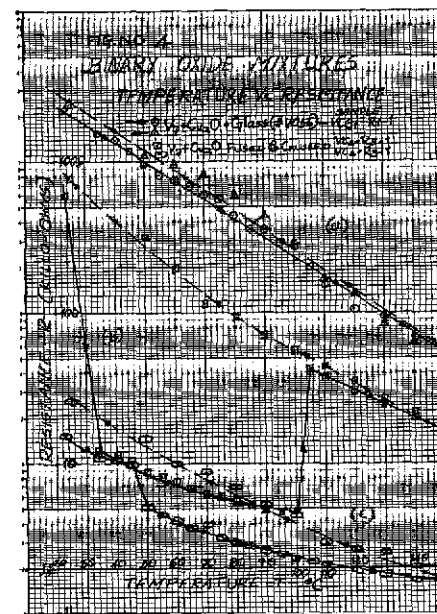


Fig. 4 Temperature-Resistance curves for mixtures of type V-7 vanadium pentoxide and cuprous oxide (a) with glass, (b) and (c) without glass

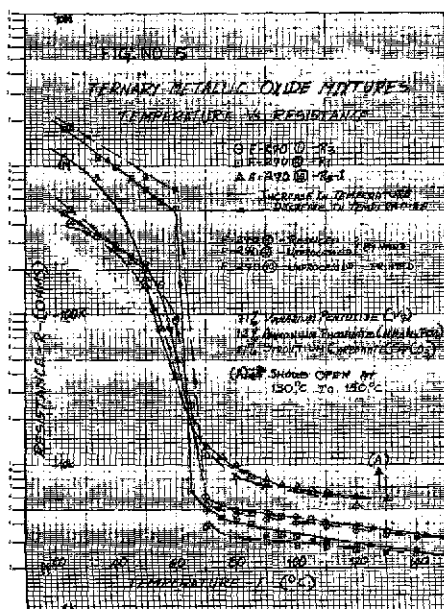


Fig. 5 Temperature characteristics of ternary mixtures (vanadium pentoxide, strontium carbonate and ammonium phosphate). Materials were applied to the substrate by hand and by screen printing.

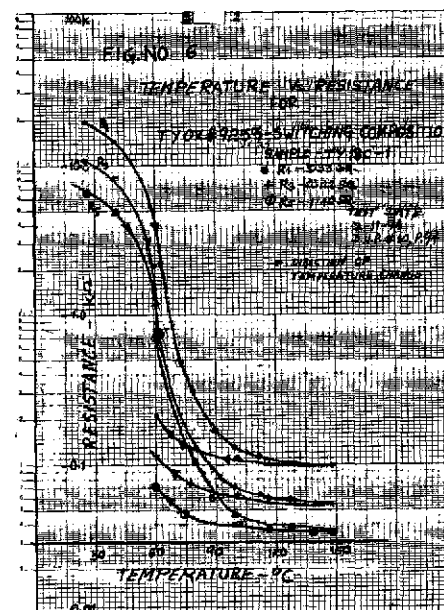


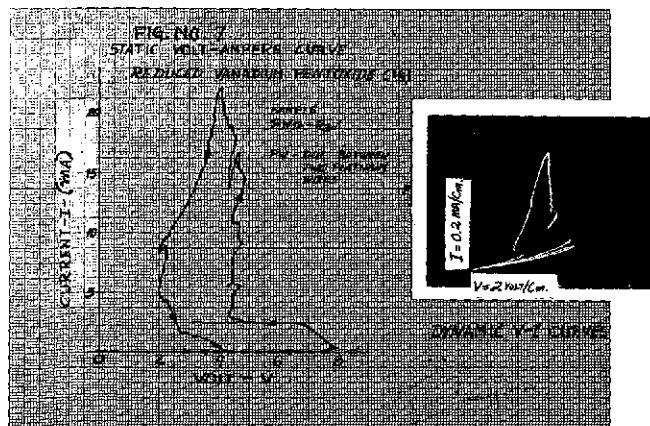
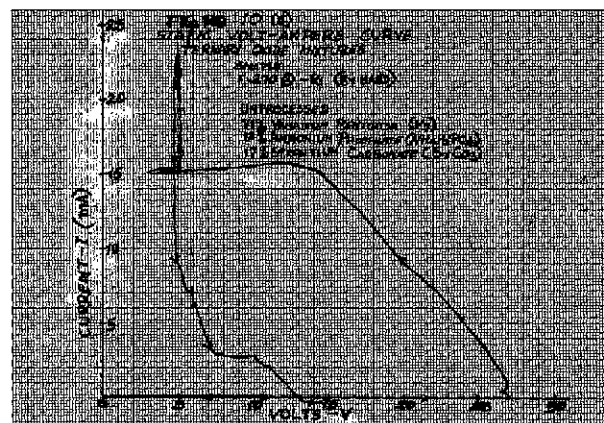
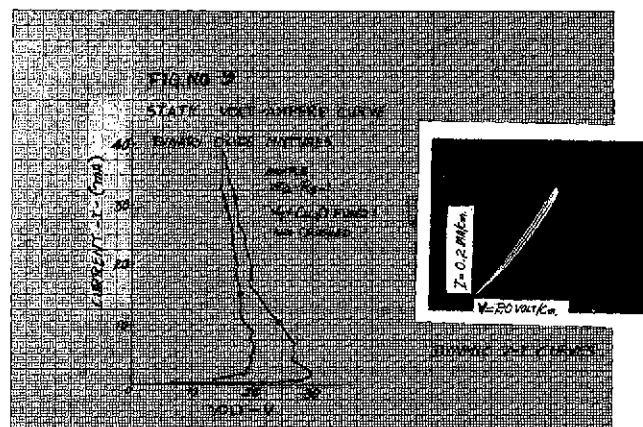
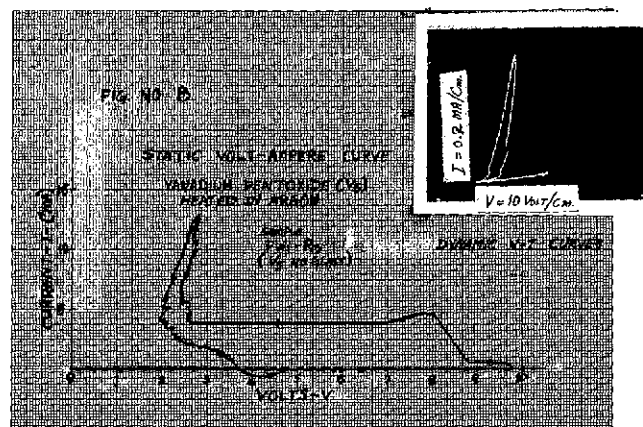
Fig. 6 Temperature-Resistance characteristics for three samples of Tyox 9253 switching composition screen printed and fired on a 96% alumina substrate.

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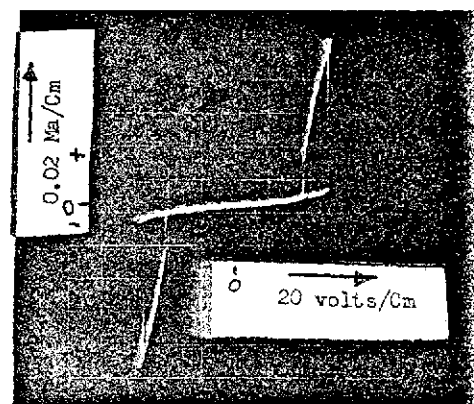
# ELECTRICAL TESTS ON OXIDE SWITCHES

Static and dynamic volt-ampere characteristics were obtained for the various samples and are indicated in Figs. 7 to 11. Static V-I curves were obtained using a circuit consisting of a 2.7K ohm limiting resistor, a 10 ohm current monitoring resistor, the oxide switch and a variable d.c. source, all connected in series. Voltages across the oxide switch and the current resistor were recorded using an X-Y plotter. Dynamic volt-ampere curves were obtained using a curve tracer and an oscilloscope camera.

Fig. 7 shows results for a reduced "PW" type sample of V-5 vanadium pentoxide on the same substrate as the sample whose temperature-resistance curve is shown in Fig. 2. Switching occurred at approximately 8 volts in the static test and at about 15 volts in the dynamic tests at a frequency of 120 Hz. Results for a similar sample heated in argon is given in Fig. 8. This is the same sample whose temperature-resistance curve is shown in Fig. 3. A relatively large voltage range over which the current is constant at about 4 milliamps is in evidence after the sample switched. The static voltages required to switch these devices varied from about 6 to 30 volts but the dynamic voltages ranged from two to about five times the corresponding static voltage. Curves for the binary oxide mixture indicated in Fig. 9 switched statically at 30 volts but did not switch at 120 volts in the dynamic test. Fig. 10 shows representative static and dynamic volt-ampere curves for the ternary oxide

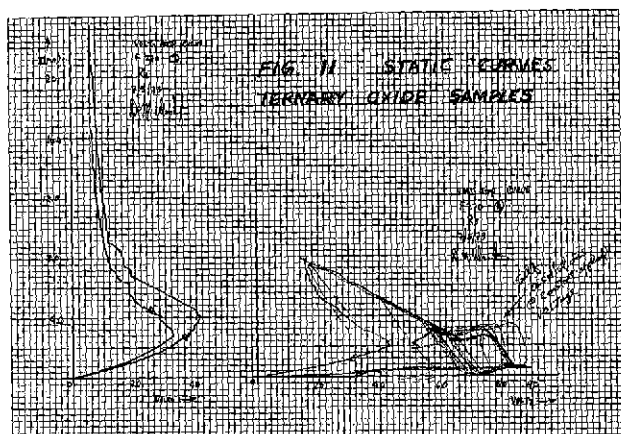


(b)  
F270-10  
R5-1



devices. The static curve (a) is for sample F-270-2-R1 applied by hand to the substrate (see Fig.5) and the dynamic curve (b) is for the screen printed sample (see Fig.5). The dynamic characteristic is for both positive and negative voltages and shows this sample to be bilateral as were all samples reported on herein.

The self oscillatory nature of some of the devices is indicated in Fig.11. This was a type "F270" ternary device which spontaneously went into self oscillation while its static curve was being recorded on an X-Y plotter as shown on the right side of the figure. This phenomenon suggests the use of these devices in oscillator circuits as will be shown later.



Since all of the volt-ampere tests depicted herein were performed at room temperature, consideration of the thermal behavior of these devices would suggest that the switching or oscillatory mode occurs when the electrical power loss in the device is sufficient to raise its temperature to the critical points indicated in the temperature-resistance plots. The power required for switching these devices can be approximated from the V-I curves to be in the order of

milliwatts and is a function of thermal conductivities of the oxide materials, terminals, the substrate and the immediate environment, etc. Switching power can be reduced by incorporating thermal bias circuits as well as decreasing the size of the devices. Switching time varied from a millisecond or less for the single oxide system to a microsecond or less for the ternary samples as indicated in the pulse tests.

The pulse test circuit diagram and representative voltage-current-time oscilloscope wave forms for some of the metallic oxide switches are shown in Fig.12. Thermal time lag after application of the voltage pulse for the single oxide "PW" device is in evidence. Such a device might switch in 3 to 5 milliseconds. Integration of the volt-ampere product curve with respect to time would give the minimum energy required for switching during single pulse application, which for this sample would be approximately 0.1 joule. It was verified by tests that the pulse switching energy required could be greatly reduced by using a d.c. source in series with the pulse generator to maintain the device at a temperature slightly below the critical temperature value. Thereafter a positive pulse would switch the device to the low resistance state and the d.c. source would maintain it in this state until a subsequent negative pulse would switch it back to the high resistance state. The device therefore could be used as a bistable resistor or as a memory element. The required thermal bias could be provided externally or by a thick film resistive heater printed directly on the substrate but electrically isolated from the switching circuit.

Pulse test wave forms for the "F270" device whose thermal characteristic is given in Fig.5 is also indicated in Fig. 12 on the right. The test was performed at room temperature without thermal bias and indicates a switching time of 3 microseconds. The minimum energy required for switching was calculated to be in the order of  $10^{-7}$  joule. Switching times and energies in these ranges suggest that the switching mechanism could be induced by strong electric field strengths coupled with thermal effects. Other researchers<sup>5</sup> who observed comparable switching times using similar materials, have advanced a theoretical explanation based on thermal considerations.

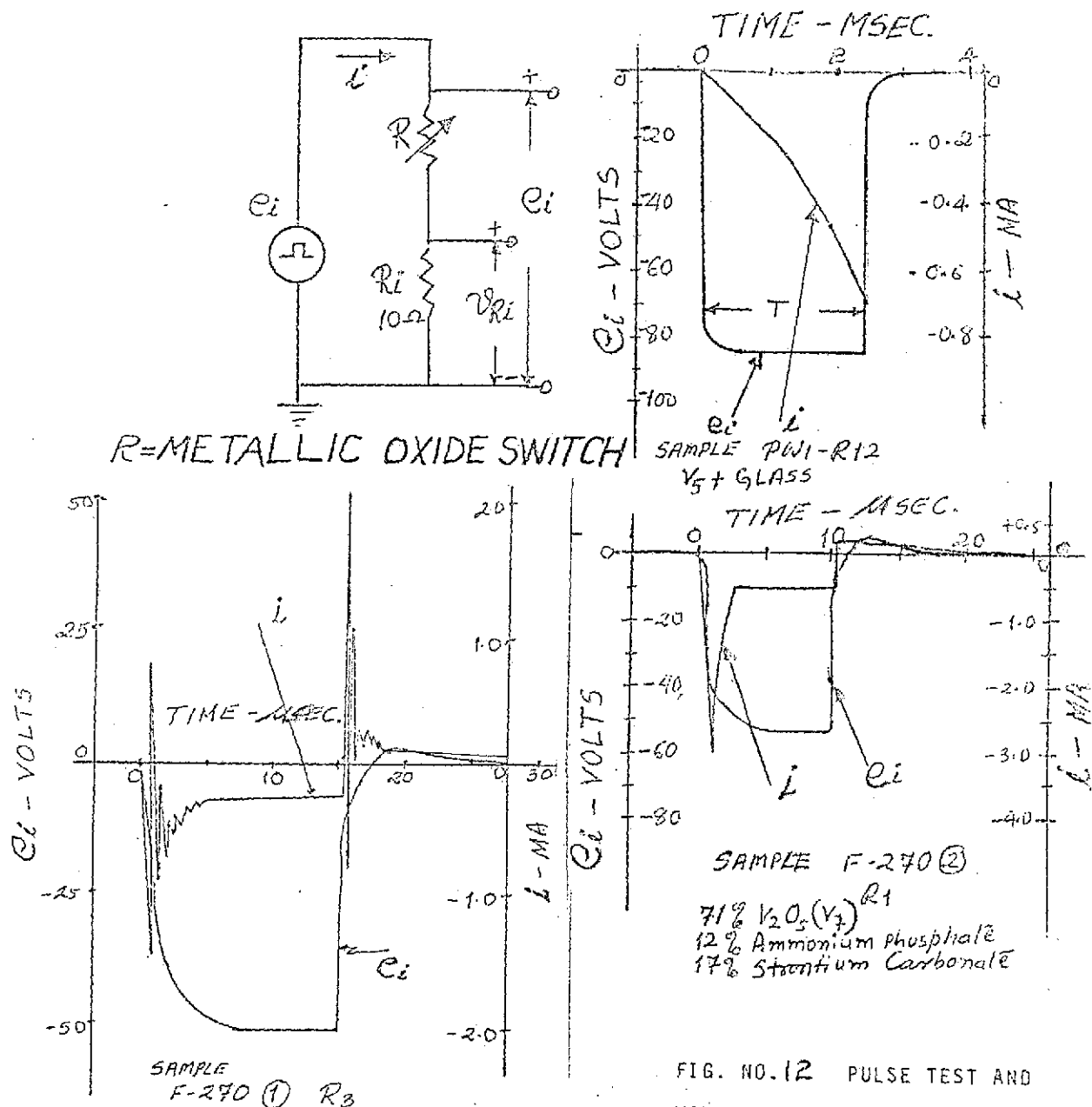


FIG. NO. 12 PULSE TEST AND  
WAVE FORMS FOR METALLIC OXIDE  
SWITCHES

#### OSCILLATOR APPLICATIONS

Both high and low frequency oscillator applications of these devices are possible as indicated by the negative resistance type self oscillations presented in Fig. 11 and the high frequency "ringing" indicated by sample F270-1-R3

in Fig. 12. This sample is equivalent to a high frequency "tank" circuit. Although the oscillations were not sustained in these cases there is evidence that the necessary conditions for sustained oscillations could be met by proper circuit

design and more accurate ambient temperature control. The experimental relaxation oscillator circuit shown in Fig.13 was set up using a single oxide system device which gave reliable sustained oscillations at frequencies ranging from 2.0 Hz. to 100 Hz. by varying the value of the capacitor.

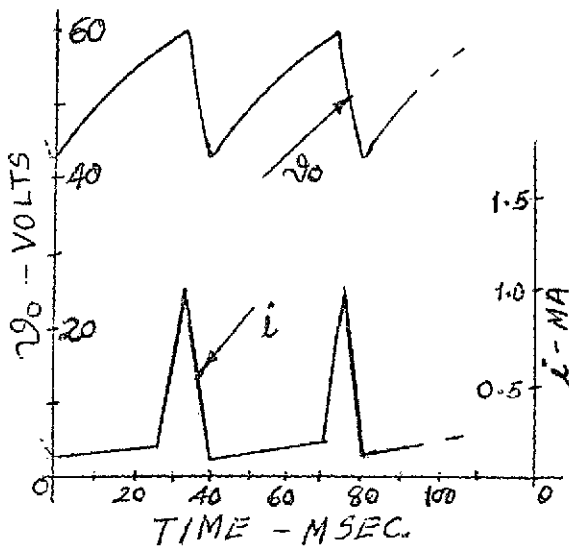
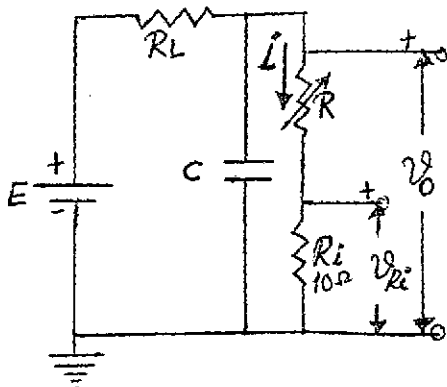


Fig.13 Relaxation oscillator circuit and wave forms. R is the metallic oxide switch, sample PW1-R51 consisting of V-5 processed in an argon atmosphere.

## SUMMARY

Practical metallic oxide switches have been processed using thick film technology. Critical switching temperatures from 30 to 130 degrees C were observed. Applications of these devices in logic and switching circuits, memory elements and oscillators are apparent. Because these devices can be made extremely small, require milliwatt to microwatt switching power with switching times in the order of a microsecond or less at voltages from 10 to 150 volts, they could be readily used in the hybrid microelectronics industry.

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